1,5-Dipolar electrocyclizations of Thiocarbonyl Ylides bearing C=N groups: Reactions of N-[(Dimethylamino)methylene]thiobenzamide and 2-(Dimethylhydrazono)-1-phenylethane-1-thione with Diazo compounds

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Abstract: The reactions of thiobenzamide 8 with diazo compounds proceeded via reactive thiocarbonyl ylides as intermediates, which underwent either a 1,5-dipolar electrocyclization to give the corresponding five-membered heterocycles, i.e., 4-amino-4,5-dihydro-1,3-thiazole derivatives (i.e., 10a, 10b, 10c, cis-10d, and trans-10d) or a 1,3-dipolar electrocyclization to give the corresponding thiiranes as intermediates, which underwent a SNi'-like ring opening and subsequent 5-exo-trig cyclization to yield the isomeric 2-amino-2,5-dihydro-1,3-thiazole derivatives (i.e., 11a, 11b, 11c, cis-11d, and trans-11d). In general, isomer 10 was formed in higher yield than isomer 11. In the case of the reaction of 8 with diazo(phenyl)methane (3d), a mixture of two pairs of diastereoisomers was formed, of which two, namely cis-10d and trans-10d, could be isolated as pure compounds. The isomers cis-11d and trans-11d remained as a mixture. In the reactions of the thioxohydrazone 9 with diazo compounds 3b and 3d, the main products were the alkenes 18 and 23, respectively. Their formation was rationalized by a 1,3-dipolar electrocyclization of the corresponding thiocarbonyl ylide and subsequent desulfurization of the intermediate thiiran. As minor products, 2,5-dihydro-1,3-thiazol-5-amines 21 and 24 were obtained, which have been formed by 1,5-dipolar electrocyclization of the thiocarbonyl ylide, followed by a 1,3-shift of the dimethylamino group.

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1,5-Dipolar Electrocyclizations of Thiocarbonyl Ylides Bearing C=N Groups: Reactions of *N* -[(Dimethylamino)methylene]thiobenzamide and 2-(Dimethylhydrazono)-1-phenylethanethione with Diazo Compounds

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The reactions of thiobenzamide **8** with diazo compounds proceeded *via* reactive thiocarbonyl ylides as intermediates, which underwent a 1,5-dipolar electrocyclization to give the corresponding five membered heterocycles, *i.e.,* 1,3-thiazole derivatives (**12a**, **12b**, **13**, **14**, and **15a**, **15b**). In the case of the reaction of **8** with phenyldiazomethane (**3b**) and diazomethane (**3c**), 2,5-dihydro-1,3-thiazoles **13** and **14**, respectively, were formed whereas the reaction of **8** with diphenyldiazomethane (**3a**) and diazocyclohexane (**3d**), respectively, led to mixtures of the corresponding 2,5- and 4,5-dihydro-1,3-thiazoles. In the reactions of the α-thioxohydrazone **9** with diazo compounds **3a** and **3b**, the main products were the alkenes **17** and **20**. Their formation was rationalized by a 1,3-dipolar electrocyclization of the corresponding thiocarbonyl ylide and subsequent desulfurization of the intermediate thiirane. As minor products, 2,5-dihydro-1,3-thiazol-5-amines **18** and **21** were obtained, which have been formed by 1,5-dipolar electrocyclization of the thiocarbonyl ylide followed by a 1,3-shift of the dimethylamino group.

1. Introduction. – The concept of the 1,5-dipolar electrocyclization as a tool for the synthesis of five-membered heterocycles was proposed 25 years ago [1][2]. Since, we have shown that thiocarbonyl ylides, which bear a carbonyl group at the C(α)-atom, undergo this cyclization to give 1,3-oxathioles [3][4] (see also [5][6]). These thiocarbonyl ylides were generated *in situ* by the reaction of thiocarbonyl derivatives with α-diazo carbonyl compounds. Very recently, we reported on the reaction of α-thioxocarbonyl derivatives with diazo compounds [7]. We were mostly interested in systems, in which the conjugated π-system consisted of a C=O or a C=S group, *i.e.*, in reactions of α-thioxoketone **1** and α-thioxothioamide **2** (*Scheme 1*).

Scheme 1

The reactions with diazo compounds **3** all followed the same pathway: 1,3 dipolar cycloaddition to give a 2,5-dihydro-1,3,4-thiadiazole, N_2 elimination by cycloreversion to produce the thiocarbonyl ylides **4a**, and 1,5-dipolar electrocyclization. The resulting products are either 1,3-oxathioles **5** and 1,3-dithioles, respectively. Some thiirane side products, which were formed by a competing 1,3-dipolar electrocyclization, were unstable, and elimination of sulfur led to the corresponding alkenes, *e.g.* **7**.

With the aim of extending the scope of this reaction, we used thiocarbonyl compounds, which possess a conjugated system containing a N-atom. Since *N*-[(dimethylamino)methylene]thiobenzamide (**8**) is not only readily available, but also stable, and thus allows for a precise calculation of the yield[2]), we used it as a starting

[2]) Because of unstable starting materials it was a problem to calculate correct yields for the reactions described in [7].

material in the present work. Because we were interested in systems with the N-atom in different positions, reactions of 2-(dimethylhydrazono)-1-phenylethanethione (**9**) were also investigated. Although **9** showed a few drawbacks concerning stability and yield calculation, we used it because of the relatively simple four-step synthesis. The results of the reactions with **8** and **9** are presented below.

2. Results and Discussion. – *Reactions with* N-*[(Dimethylamino)methylene]-thiobenzamide* (**8**). The reaction of **8** with diphenyldiazomethane (**3a**) was carried out in CH_2Cl_2 at room temperature in the presence of a catalytic amount of $Rh_2(OAc)_4$ and yielded two products. Based on the previous experiences from experiments with thiocarbonyl ylides [7], we assumed that the reaction would lead to an intermediate thiocarbonyl ylide **4a**, which would undergo either a 1,3-dipolar electrocyclization to give the thiirane **10** and, by subsequent desulfurization, the alkene **11**, or a 1,5-dipolar electrocyclization to give the corresponding 1,3-thiazol **12a** (*Scheme 2*).

Scheme 2

The ^{13}C-NMR spectra of the two isolated products showed that we could exclude structure **10** and **11**, because the expected *d* for the amidine C-atom at about 100 ppm was missing (see experimental part). The spectra of both compounds were very similar with only small deviations of 5-10 ppm for some signals, which indicated that the substances could be the tautomers **12a** and **12b**. NOE-experiments of the two tautomers have shown that the Me_2N group in **12a** has to be close to the H-atom, which absorbed at 6.84 ppm. In the case of **12b**, the analogous NOE-experiments showed no response of an H-atom bonded to the heterocycle. Further confirmation was acquired from the MS spectra, in which the molecular ion peaks for **12a** and **12b**

were identical. Unfortunately it was not possible to crystallize the two products as they remained as oily substances. It seems that *N*,*N*-dimethyl-*N*-(2,5,5-triphenyl-2,5-dihydrothiazol-4-yl)amine (**12b**) is slightly more stable than the 4,5-dihydro isomer (**12a**); the corresponding yields were 49% and 30%, respectively.

The analogous reaction of **8** with phenyldiazomethane (**3b**) in THF led to only one product. Based on the ^{13}C-NMR data (*s* at 166.9 ppm, *d* at 104.9 ppm), the 4,5-dihydro-1,3-thiazole structure **13** was assigned to the product (*Scheme 3*).

Scheme 3

It has to be mentioned that only one of the two possible stereoisomers was isolated. With respect to the thermodynamic stability, the *trans*-product should be more stable than the *cis*-isomer. On the other hand, the coupling constant between H-C(4) and H-C(5) of 4.3 Hz could indicate the *cis*-configuration for the following reasons. As a rule, the *cis* coupling in five-membered heterocycles is larger than the *trans* coupling [8]. As in the analogous compound **14** (*Scheme 3*) H-C(4) appears as *dd* with J = 5.2 and 1.9 Hz, we assume that J(*cis*) in this ring system is *ca*. 5 Hz, which corresponds reasonably well with J = 4.3 Hz found in **13**. An explanation of the preferred formation of the thermodynamically less favored *cis*-isomer is based on the selectivity rules for pericyclic reactions (see for example [9][10]). For steric reasons, the preferred structure of the thiocarbonyl ylide formed from **8** and **3b** should be **4b'**, which is in equilibrium with **4b** (*Scheme 4*). The disrotatory ring closure of the latter yields then **13**. The more stable *trans*-isomer **13'** could be formed *via* enolization,.

Scheme 4

Similar to the reaction of **8** with **3b**, treatment with CH_2N_2 (**3c**) led to a single product **14** (*Scheme 3*). In contrast to the previous experiments, the reaction takes place spontaneously and, therefore, there was no need to add Rh-catalyst.

The next diazo compound, which was selected for the reaction with **8**, was diazocyclohexane (**3d**). In CH_2Cl_2 at room temperature, a spontaneous reaction occurred and gave a mixture of two products. In the crude NMR spectrum, the products showed the already known pattern of the **12a/12b** mixture, but the ratio of **15a** to **15b** rose to 3:1 (*Scheme 3*). The latter proved to be unstable and could not be isolated in pure form.

The assignment of the structure of **15a** was based again on the absorptions of C(2) and C(4) in the ^{13}C-NMR spectrum (*s* at 167.4 ppm, *d* at 101.5 ppm). It is not possible to give an explanation for the different results with **3a**, **3d** and **3b**, **3c** on the basis of electronic arguments, since the electronic effects of the substituents do not correlate with the reaction outcome. On the other hand, a correlation on steric grounds is possible, namely, with the increasing bulkiness of the substituents in the diazo component, the amidine structure is preferred.

Surprisingly, the reaction of ethyl diazoacetate (**3e**) with **8** did not lead to the expected thiazole derivative. The only product, which could be isolated in traces, was **16**, the 'trimer' of the starting diazo compound. Its structure was established by X-ray crystallography (*Fig. 1*). In the crystal structure, the two ester groups at the adjacent chiral centres have the *trans* configuration. The NH group forms an intermolecular H-bond with one of the ester carbonyl O-atoms of an adjacent molecule and thereby links the molecules into extended chains, which run parallel to the [100] direction and can be described by a graph set motif [11] of C(6).

Fig. 1

The described results obtained with **8** show that this starting material is relatively unreactive and, therefore, the reaction with less reactive diazo compounds has to be catalyzed by $Rh_2(OAc)_4$. Whereas in the reaction of **8** with **3c**, 11% of the product could be isolated, no reaction took place with **3a** and **3b** without addition of catalyst. In the case of **3e**, no formation of a thiocarbonyl ylide was observed. Instead, dimerization of the generated carbenoïd yields diethyl fumarate [13], which undergoes a 1,3-dipolar cycloaddition with **3e** to give **16**.

2.2. *Reactions with 2-(Dimethylhydrazono)-1-phenylethanethione* (**9**). The reaction of **9** with **3a** in benzene at room temperature gave two products. The first one was identified as *N*,*N*-dimethyl-*N'*-(2,3,3-triphenylprop-2-enylidene)hydrazine (**17**). The reaction mechanism of its formation, in analogy with previous cases, is supposed as follows: 1,3-dipolar cycloaddition and elimination of N_2 yields the thiocarbonyl ylide **4c**, which undergoes a 1,3-dipolar electrocyclization to give the corresponding thiirane **22**. Finally, desulfurization of the latter leads to **17** (*cf.* [7]). The second product was isolated in small yields and turned out, surprisingly, to be *N*,*N*-dimethyl-*N*-(2,2,5-triphenyl-2,5-dihydrothiazol-5-yl)amine (**18**). It apparently results from a rearrangement of the primarily formed intermediate 3-amino-1,3-thiazole **19**. In this case, unlike in the reactions with **8**, the dimethylamino group is bound to the N(3) atom. A 1,3-shift of the amino substituent then leads to the 2,5-dihydro-1,3-thiazol **18** (*Scheme 5*).

Scheme 5

The structures of **17** and **18** have been established by X-ray crystallography (*Fig. 2*). The conjugated π-system in **17** from C(1) to N(4), including N(5), C(7), C(13), and C(19) is almost planar. All phenyl substituents in compound **17** are twisted out of this plane because of steric reasons (torsion angles C(2)-C(1)-C(7)-C(8) 52.7(2)°, C(2)-C(1)-C(13)-C(18) 44.0(2)°, and C(1)-C(2)-C(19)-C(20) 55.1(2)°). In the case of **18**, the asymmetric unit contains two symmetry-independent molecules, each of which is disordered by inversion of the entire molecule about its centre of gravitiy. The ratio of the major orientation of each molecule to the minor orientation is about 93:7. The crystals are also inversion twins.

Fig. 2

The analogous reaction of **9** with **3b** gave a complex mixture of products, which consisted of at least two pairs of diastereoisomers. The (*E*/*Z*)-isomers of *N*,*N*-dimethyl-*N'*-(2,3-diphenylprop-2-enylidene)hydrazine (**20**) and the *cis*/*trans*-isomers of *N,N*-dimethyl-*N*-(2,5-diphenyl-2,5-dihydrothiazol-5-yl)amine (**21a,b**) are the likely products, which could be separated partially by CC and MPLC. The structures were elucidated on the basis of the NMR and mass spectra. Furthermore, one of the diastereoisomers of **21a,b,** *i.e. trans*-**21**, could be crystallized and the X-ray crystal-structure was determined successfully. In the crystal, the heterocyclic ring has a shallow envelope conformation with S(3) as the envelope flap. The phenyl substituents lie *cis* to one another.

Fig. 3

The reactions of **9** with **3a** and **3b**, respectively, showed that the intermediate thiocarbonyl ylide **4c** reacts only to a minor extent to give the 5-membered ring. The preferred reaction of **4c** is the 1,3-dipolar electrocyclization which leads to an intermediate thiirane **22** and subsequent desulfurization yields the alkenes.

3. Conclusion. – The presented results show that the two thiocarbonyl compounds **8** and **9** with a conjugated C=N group react with diazo compounds **3** to give the corresponding thiocarbonyl ylides of type **4** with an extended π-system. In the cases of **8** and the less reactive **3a** and **3b**, the reaction has to be catalyzed by $Rh_2(OAc)_4$. Whereas in the non-catalyzed reaction a 1,3-dipolar cycloaddition to give the corresponding 2,5-dihydro-1,3,4-thiadiazole and subsequent N_2-elimination is the likely reaction mechanism for the formation of the thiocarbonyl ylide, an initial Rh-catalyzed N_2-elimination to give a carbenoïd, which adds to the C=S group, leads to the intermediate 1,3-dipoles in the catalyzed reactions [5][6]. The thiocarbonyl ylides of type **4a**, which have been generated from **8**, undergo preferentially a 1,5-dipolar electrocyclization and yield dihydro-1,3-thiazole derivatives. On the other hand, the main reaction of the isomeric thiocarbonyl ylides **4c** is the 1,3-dipolar electrocyclization, which leads to thiiranes **22**.

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Experimental Part

1. *General.* See [7]. IR Spectra in KBr unless otherwise stated. ^{1}H- and ^{13}C-NMR Spectra: *Avance DRX-500* (500 and 125 MHz, resp.), and *Avance DRX-600* (600 and 150 MHz, resp.). M.p.: *Büchi* B-540.

2. *Starting Materials.* All thiocarbonyl derivatives and their precursors and all diazo compounds were prepared following known protocols: diphenyldiazomethane (**3a**) [14], phenyldiazomethane (**3b**) [15], diazomethane (**3c**) [16], diazocyclohexane (**3d**) [17], *N*-[(dimethylamino)methylene]thiobenzamide (**8**) [18], 2-(dimethylhydrazono)-1-phenylethanethione (**9**) [19][20]. All other reagents are commercially available.

3. *Yields*. As **9** and almost all diazo compounds are only stable in solution and the diazo compounds were often used in excess, the yields of the corresponding reactions were approximated. They are based on experience [7] or on the volume of N_2 evolved.

4. *General Procedure A* (*GP A*): To a soln. of a thiocarbonyl compound (1.8-3 mmol) in CH_2Cl_2 or THF (20-100 ml), the diazo compound (3-7 mmol) in toluene, benzene, or Et_2O (30-130 ml) was added in several portions by means of a dropping funnel, or, in the case of **3c,** by means of a *Pasteur* pipette. After total conversion of the thiocarbonyl compound, monitored either by TLC, color change or evolution of N_2[3]), the solvent was evaporated and the mixture was analyzed and purified by chromatography using silica gel, which had been treated with 3% Et_3N. Furthermore, the solvent was doped with 1% of Et_3N.

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[3]) The evolution of N_2 was determined volumetrically using a gas burette attached to the reaction vessel.

5. *Reaction of* N-*[(Dimethylamino)methylene]thiobenzamide* (**8**) *with diazoalkanes.*

5.1. N,N-*Dimethyl*-N-*(2,5,5-triphenyl-4,5-dihydro-1,3-thiazol-4-yl)amine* (**12a**) *and* N,N-*Dimethyl*-N-*(2,5,5-triphenyl-2,5-dihydro-1,3-thiazol-4-yl)amine* (**12b**). According to *GP A,* a suspension of **8** (360 mg, 1.87 mmol) in CH_2Cl_2 (20 ml) and a soln. of **3a** (*ca*. 2.5 mmol) in benzene (20 ml) were used. To the stirred mixture at r.t., a catalytic amount (20 mg) of $Rh_2(OAc)_4$ was added. After *ca.* 16 h, the mixture was separated by CC (hexane/AcOEt 20:1 to 5:1): 200 mg (0.56 mmol, 30%) of **12a** and 328 mg (0.92 mmol, 49%) of **12b**. Data of **12a**: Yellowish oil. R_f = 0.3; hexane/AcOEt 8:1. IR: 3056*m*, 3028*w*, 2977*m*, 2942*m*, 2860*m*, 2825*m*, 2779*m*, 1807*w*, 1734*w*, 1680*w*, 1624*s*, 1599*s*, 1545*m*, 1489*s*, 1470*s*, 1445v*s*, 1352*s*, 1289*m*, 1257*s*, 1205*m*, 1179*s*, 1152*m*, 1081*s*, 1067*s*, 1043*s*, 1023v*s*, 1002*s*, 932*m*, 908*w*, 852*s*, 824*w*, 772*s*, 758*s*, 742v*s*, 695v*s*, 639*m*. ^{1}H-NMR: 7.52–7.49 (*d*-like, 2 arom. H); 7.40–7.35 (*t*-like, 4 arom. H); 7.21–7.00 (*m*, 9 arom. H); 6.84 (*s*, HC(4)); 2.27 (*s*, Me_2N). ^{13}C-NMR: 171.2 (*s*, C(2)); 143.1, 142.8, 133.2 (3*s*, 3 arom. C); 130.5, 130.2, 129.4, 129.0, 128.0, 127.8, 127.7, 127.0, 126.9 (9*d*, 15 arom. CH); 101.5 (*d*, C(4)); 78.3 (*s*, C(5)); 39.8 (*q*, Me_2N). CI-MS (NH_3): 359 (10, $[M + 1]^+$), 327 (100, $[M – S + 1]^+$), 314 (5 $[M – Me_2NH]^+$), 193 (22).

Data of **12b**: Yellowish oil. R_f = 0.5; hexane/AcOEt 8:1. IR: 3057*m*, 3027*m*, 2935*s*, 2865*s*, 2831*s*, 2786*m*, 1805*w*, 1733*w*, 1596*s*, 1575*s*, 1491v*s*, 1472*m*, 1445v*s*, 1311*m*, 1275*s*, 1227*s*, 1176*m*, 1156*m*, 1083*s*, 1062v*s*, 1040v*s*, 994v*s*, 944v*s*, 920*m*, 901*m*, 888*m*, 828*m*, 765v*s*, 752v*s*, 723v*s*, 694v*s*, 632*m*, 623*s*. ^{1}H-NMR: 7.87–7.84 (*q*-like, 2 arom. CH); 7.43–7.07 (*m*, 13 arom. CH); 6.01 (*s*, HC(2)); 2.19 (*s*, Me_2N). ^{13}C-NMR: 166.1 (*s*, C(4)); 149.1, 140.1, 133.2 (3*s*, 3 arom. C); 131.4, 129.9, 128.5, 128.3, 128.3, 127.3, 126.9, 126.9, 126.4 (9*d*, 15 arom. CH); 100.9 (*d*, C(2)); 74.4 (*s*, C(5)); 41.3 (*q*, Me_2N). CI-MS (NH_3): 359 (100, $[M + 1]^+$), 314 (39, $[M – Me_2NH]^+$), 224 (37).

5.2. N,N-*Dimethyl*-N-*(*cis-*2,5-diphenyl-4,5-dihydro-1,3-thiazol-4-yl)amine* (**13**). According to *GP A,* soln. of **8** (592 mg, 3 mmol) in dry THF (20 ml) and **3b** (*ca*. 4 mmol) in toluene (80 ml) were used. To the stirred mixture at r.t., a catalytic amount (20 mg) of $Rh_2(OAc)_4$ was added. After 4 d, the mixture was separated by CC (hexane/AcOEt 4:1 to 1:4): 258 mg (*ca.* 41%[4])) of **13**. Yellowish-oily crystals. M.p. not measurable. IR (film): 3083*m*, 3061*s*, 3028*s*, 2972*s*, 2940*vs*, 2866*s*, 2833*s*, 2788*s*, 1808*w*, 1754*w*, 1716*w*, 1687*w*, 1608*vs*, 1600*vs*, 1579*s*, 1492*vs*, 1473*s*, 1449*vs*, 1361*s*, 1293*s*, 1272*s*, 1253*s*, 1228*s*, 1177*m*, 1158*s*, 1075*s*, 1040*vs*, 997*vs*, 960*s*, 936*s*, 865*m*, 766*vs*, 751*m*, 690*vs*. ^{1}H-NMR: 7.87–7.84 (*d*-like, 2 arom. H); 7.42–7.32 (*m*, 3 arom. H); 7.25–7.17 (*m*, 5 arom. H); 5.46 (*d*, *J* = 4.3, HC(4)); 4.76 (*d*, *J* = 4.3, H(C(5)), 2.39 (*s*, Me_2N). ^{13}C-NMR: 166.9 (*s*, C(2)); 141.8, 130.6 (2*s*, 2 arom. C); 131.9, 127.9, 127.6[5]), 126.6, 126.5 (5*d*, 10 arom. CH); 104.9 (*d*, C(4)); 54.6 (*d*, C(5)); 39.4 (*q*, Me_2N). CI-MS (NH_3): 284 (21), 283 (100, $[M + 1]^+$), 238 (45, $[M - Me_2NH + 1]^+$), 148 (21).

5.3. N,N-*Dimethyl*-N-*(2-phenyl-4,5-dihydro-1,3-thiazol-4-yl)amine* (**14**). According to *GP A,* soln. of **8** (385 mg, 2 mmol) in THF (20 ml) and **3c** (*ca*. 5 mmol) in Et_2O (20 ml) were used. After 3 d at r.t., the mixture was separated by CC (hexane/AcOEt 8:1 to 1:1): 45 mg (*ca.* 11%) of **14**. Yellowish crystals. M.p. 64–67°. IR: 3126*w*, 3058*m*, 3032*w*, 2922*m*, 2805*w*, 1726*m*, 1683*m*, 1644v*s*, 1579*m*, 1489*s*, 1445*s*, 1414*s*, 1354*m*, 1274*m*, 1254*m*, 1226*m*, 1185*m*, 1159*w*, 1116*m*, 1061*s*, 1042*s*, 1030*s*, 1009*m*, 775*s*, 746*s*, 732*s*, 696*s*. ^{1}H-NMR: 7.95–7.92 (*d*-like, 2 arom. H); 7.49–7.40 (*m*, 3 arom. H);

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[4]) *Ca*. 160 mg of the starting material **8** were recovered.

[5]) The intensity of this signal indicates absorption of 4 arom. CH.

7.08 (*dd*, *J* = 5.2, 1.9, HC(4)); 4.34 (*dd*, *J* = 16.3, 1.9, 1H of CH_2); 4.22 (*dd*, *J* = 16.3, 5.2, 1H of CH_2); 2.25 (*s*, Me_2N). ^{13}C-NMR: 168.9 (*s*, C(2)); 133.1 (*s*, 1 arom. C); 131.4, 128.5, 128.5 (3*d*, 5 arom. CH); 107.3 (*d*, C(4)); 41.3 (*t*, CH_2); 39.0 (*q*, Me_2N). CI-MS (NH_3): 206 (18, $M^{+\cdot}$), 174 (100, $[M - S]^+$), 161 (94, $[M - Me_2N]^+$), 134 (82, $[M - NHCHNMe_2]^+$), 103 (58, $PhCN^{+\cdot}$).

5.4. N,N-*Dimethyl*-N-*(2-phenyl-1-thia-3-azaspiro[4.5]dec-2-en-4-yl)amine* (**15a**). According to *GP A,* a suspension of **8** (384 mg, 2 mmol) in CH_2Cl_2 (10 ml) and a soln. of **3d** (*ca*. 2.5 mmol) in CH_2Cl_2 (40 ml) were used. After 1 d at r.t., the mixture was separated by CC (hexane/AcOEt 10:1 to 5:1): 360 mg (67%) of **15a** and 120 mg (22%) of a mixture of **15a** and the 3-ene tautomers **15b**[6]). Data of **15a**: Yellowish oil. IR (film): 3061*m*, 3027*w*, 2930*vs*, 2855*vs*, 2833*vs*, 2790*s*, 2669*w*, 1808*w*, 1756*w*, 1688*w*, 1595*vs*, 1577*s*, 1491*m*, 1473*s*, 1447*vs*, 1404*w*, 1377*m*, 1295*s*, 1266*vs*, 1246*vs*, 1229*s*, 1212*m*, 1176*m*, 1156*m*, 1135*m*, 1091*s*, 1074*s*, 1042*vs*, 1025*vs*, 993*vs*, 958*s*, 940*s*, 909*m*, 858*s*, 766*vs*, 690*vs*, 625*m*. ^{1}H-NMR: 7.91–7.88 (*d*-like, 2 arom. H); 7.45–7.36 (*m*, 3 arom. H); 4.92 (*s*, HC(4)); 2.48 (*s*, Me_2N) 2.04–1.32 (*m*, 10 H, cyclohexyl). ^{13}C-NMR: 167.4 (*s*, C(2)); 133.8 (*s*, 1 arom. C); 131.0, 128.3, 128.1 (3*d*, 5 arom. CH); 101.5 (*d*, C(4)); 66.6 (*s*, C(5)); 42.3 (br. *q*, Me_2N); 40.9, 32.2, 26.3, 25.5, 24.2 (5*t*, 5 CH_2, cyclohexyl). EI-MS: 275 (10), 274 (47, $M^{+\cdot}$), 230 (7, $[M - Me_2N]^+$), 171 (28), 160 (100 $[M - S - cyclohexyl]^+$), 138 (18), 121 (11), 103 (24), 57 (84).

Data of **15b** (from a *ca.* 1:3 mixture of **15a/15b**). ^{1}H-NMR: 7.48-7.38 (*m*, 5 arom. H); 6.76 (*s*, HC(2)); 2.31 (*s*, Me_2N); 1.93-1.59 (*m*, 10 H, cyclohexyl). ^{13}C-NMR: 176.8 (*s*, C(4)); 135.0 (*s*, 1 arom. C); 129.0, 128.2, 127.9 (3*d*, 5 arom. CH); 100.3 (*d*, C(2)); 72.7 (*s*, C(5)); 39.3 (*s*, Me_2N); 38.1, 36.9, 25.2, 25.0, 24.5 (5*t*, 5 CH_2, cyclohexyl).

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[6]) It was not possible to isolate **15b** in a pure form.

5.5. *Experiment with Ethyl Diazoacetate* (**3e**). According to *GP A,* a suspension of **8** (380 mg, 2 mmol) in THF (20 ml) and a soln. of **3e** (*ca*. 4 mmol) in CH_2Cl_2 (40 ml) were used. To the stirred mixture, a catalytic amount (*ca.* 20 mg) of $Rh_2(OAc)_4$ was added. After 10 d at r.t., the mixture was separated by CC (hexane/AcOEt 4:1): 450 mg of a complex mixture of products resulting from decomposition and *ca.* 15 mg triethyl *trans*-4,5-dihydro-1*H*-pyrazole-3,4,5-tricarboxylate (**16**).

Crystals suitable for an X-ray crystal-structure determination were grown from CH_2Cl_2/pentane by slow evaporation of the solvent.

6. *Reactions of 2-(Dimethylhydrazono)-1-phenylethanethione* (**9**) *with Diazoalkanes.*

6.1. N,N-*Dimethyl*-N*'-(2,3,3-triphenylprop-2-enylidene)hydrazine* (**17**) *and* N,N-D*imethyl*-N-*(2,2,5-triphenyl-2,5-dihydro-1,3-thiazol-5-yl)amine* (**18**). To a soln. of freshly prepared **9** (*ca.* 1.6 mmol) in benzene (10 ml), a purple soln. of **3a** (*ca.* 2.5 mmol) in benzene (20 ml) was added drop-wise. After stirring for 1 h at r.t., purification of the crude mixture by SC (hexane/AcOEt 15:1) and MPLC (hexane/MeOH 90:5) afforded a mixture of two products, which were separated by crystallization from hexane/AcOEt/Et_2O affording 234 mg of **17** (30%) and 60 mg (7%) of **18**. Data of **17**: Pale-brownish crystals. M.p. 176–177°. IR: 3056*w*, 3027*w*, 2992*w*, 2970*w*, 2947*m*, 2867*m*, 2828*m*, 2783*w*, 1805*w*, 1664*m*, 1596*w*, 1580*w*, 1558*w*, 1488*s*, 1467*m*, 1445v*s*, 1175*m*, 1082*m*, 1073*m*, 1033*m*, 1009v*s*, 932*m*, 923*m*, 902*s*, 873*m*, 758v*s*, 697v*s*, 648*s*, 637*s*. ^{1}H-NMR: 7.36–6.85 (*m*, 15 arom. H and 1 =CH); 2.72 (*s*, Me_2N). ^{13}C-NMR: 142.8, 142.4, 139.5 (3*s*, 3 arom. C); 137.8 (*s*, 1 =C); 136.5 (br. *s*, 1 =C, 1 =CH); 131.7, 131.0, 130.9, 127.9, 127.2, 127.1, 126.2, 126.0 (8*d*, 15 arom. CH); 42.6 (*q*, Me_2N). CI-MS (NH_3): 327 (100, $[M + 1]^+$), 284 (16, $[M - Me_2N + 1]^+$), 203 (12), 178 (19), 160 (15), 158 (13).

Crystals suitable for an X-ray crystal-structure determination were grown from hexane/AcOEt/Et_2O by slow evaporation of the solvent.

Data of **18**: Colorless crystals. M.p. 135–137°. IR: 3063*w*, 3026*w*, 2992*w*, 2970*m*, 2946*m*, 2868*m*, 2828*m*, 2783*w*, 1956*w*, 1804*w*, 1664*m*, 1595*m*, 1580*w*, 1487*s*, 1467*s*, 1445v*s*, 1031*m*, 1009v*s*, 932*m*, 923*m*, 901v*s*, 873*m*, 757v*s*, 697v*s*, 661*m*, 648*s*, 637*s*, 615*m*. ^{1}H-NMR: 7.75 (*d*-like, 2 arom. H); 7.68–7.64 (*d*-like, 2 arom. H); 7.35–7.15 (*m*, 11 arom. H, HC(4)); 2.09 (*s*, Me_2N). ^{13}C-NMR: 162.7 (*d*, HC(4)); 146.2, 145.2, 139.8 (3*s*, 3 arom. C); 128.7, 128.5, 128.3, 127.9, 127.1, 127.1, 126.9, 126.5 (8*d*, 15 arom. CH); 106.7 (*s*, C(2)); 97.5 (*s*, C(5)); 41.2, 41.1 (2*q*, Me_2N). CI-MS (NH_3): 358 (5, $M^{+\cdot}$), 327 (10, $[M - Me_2N + NH_4]^+$), 314 (28, $[M - Me_2N]^+$), 178 (100).

Crystals suitable for an X-ray crystal-structure determination were grown from $CDCl_3$ by slow evaporation of the solvent.

6.2. (E/Z)-N,N-*Dimethyl*-N*'-(2,3-diphenylprop-2-enylidene)hydrazine* (**20**) *and* N,N-*Dimethyl*-N-*(2,5-diphenyl-2,5-dihydrothiazol-5-yl)amine* (**21**). To a soln. of freshly prepared **8** (*ca.* 5 mmol) in a mixture of hexane and AcOEt (300 ml, 10:1), a soln. of **3b** (*ca.* 6 mmol) in toluene (150 ml) was slowly added at r.t.. Purification of the crude mixture after 1 h by SC (hexane/AcOEt 10:1 to 3:1) and MPLC (hexane/AcOEt 90:5) afforded 3 almost pure compounds: 163 mg and 54 mg, respectively, of the (*E*)- and (*Z*)-isomer of **20** (*i.e.* **20a** and **20b**)[7]) and 75 mg of one of the diastereoisomers of **21**. Data of **20a**: Yellowish oil. IR: 3019*m*, 2950*m*, 2851*m*, 2824*m*, 2786*m*, 1626*m*, 1593*m*, 1551*s*, 1491*s*, 1469*s*, 1446*s*, 1266*s*, 1129*m*, 1077*m*, 1043v*s*, 896*m*, 862*m*, 760*s*, 750*s*, 698v*s*, 607*m*. ^{1}H-NMR: 7.96 (*s*, CH=N); 7.88–7.59 (*m*, 10 arom. H); 7.06

[7]) It was not possible to assign the spectra to (*E*)- and (*Z*)-**20** on the basis of the present information.

(*s*, CH=C); 3.24 (*s*, Me_2N). ^{13}C-NMR: 161.9 (*d*, CH=N); 141.2, 139.6, 137.5 (3*s*, 2 arom. C, 1 =C); 132.1, 130.2, 129.3, 127.8, 127.6, 127.2, 126.9 (7*d*, 10 arom. CH, 1 =CH); 42.6 (*q*, Me_2N). CI-MS (NH_3): 252 (20), 251 (100, $[M + 1]^+$), 210 (16, $[M - Me_2N_2 + NH_4]^+$), 209 (99, $[M - Me_2N_2 + NH_3]^+$).

Data of **20b**: Colorless oil. IR: 3055*m*, 3022*m*, 2951*m*, 2854*m*, 2784*m*, 1595*m*, 1553*s*, 1444*s*, 1361*m*, 1272*s*, 1133*s*, 1040v*s*, 918*m*, 897*m*, 849*m*, 778*m*, 756v*s*, 703v*s*, 632*m*, 601*s*. ^{1}H-NMR: 7.70–7.54 (*m*, 5 arom. H); 7.53 (*s*, CH=N); 7.46-7.39 (*m*, 3 arom. H); 7.29-7.26 (*m*, 2 arom. H); 7.06 (*s*, CH=C); 3.21 (*s*, Me_2N). ^{13}C-NMR: 140.2, 139.1, 138.1 (3*s*, 2 arom. C, 1 =C); 137.0 (*d*, CH=N); 129.9, 129.8, 129.4, 128.2, 127.8, 127.0, 126.5 (7*d*, 10 arom. CH, 1 =CH); 42.7 (*q*, Me_2N). CI-MS (NH_3): 252 (19), 251 (100, $[M + 1]^+$), 223 (11, $[M - Me_2N + NH_4]^+$).

Data of *trans*-**21**: Colorless crystals. M.p. 86–88°. IR: 3080*w*, 3058*m*, 3024*m*, 2986*m*, 2959*m*, 2897*w*, 2843*w*, 2816*s*, 2772*s*, 1655*s*, 1595*w*, 1580*w*, 1488*s*, 1469*m*, 1451v*s*, 1427*m*, 1253*m*, 1235*s*, 1154*m*, 1095*m*, 1082*m*, 1064*s*, 1042*m*, 1028*m*, 996v*s*, 979*s*, 943*m*, 923*s*, 911*s*, 857*m*, 844*s*, 780*w*, 754v*s*, 732v*s*, 695v*s*, 633v*s*, 613*s*. ^{1}H-NMR: 8.02–8.00 (*d*-like, 2 arom. H); 7.99–7.50 (*m*, 6 arom. H); 7.49 (*d*, J = 2.9, HC(4)); 7.48–7.37 (*m*, 2 arom. H); 6.79 (*d*, J = 2.9, HC(2)); 2.39 (*s*, Me_2N). ^{13}C-NMR: 165.7 (*d*, C(4)); 141.0, 140.4 (2*s*, 2 arom. C); 128.7, 128.5, 128.5, 128.2, 127.9, 126.7 (6*d*, 10 arom. CH); 106.7 (*s*, C(5)); 83.5 (*d*, HC(2)); 40.6 (*q*, Me_2N). CI-MS (NH_3): 283 (10, $[M + 1]^+$), 251 (12, $[M - S + 1]^+$), 238 (100, $[M - Me_2N]^+$), 178 (88, $[M - PhCN]^+$).

Crystals suitable for an X-ray crystal-structure determination were grown from CH_2Cl_2/hexane by slow evaporation of the solvent.

7. *X-Ray Crystal-Structure Determination of* **16**, **17**, **18**, and *trans*-**21** (*Table* and *Figs. 1-3*)[8]). All measurements were performed on a *Nonius KappaCCD* diffractometer [21] using graphite-monochromated MoK_α radiation (λ 0.71073 Å) and an *Oxford Cryosystems Cryostream* 700 cooler. The data collection and refinement parameters are given in the *Table*, and views of the molecules are shown in *Figs. 1-3*. Data reduction was performed with *HKL Denzo* and *Scalepack* [22]. The intensities were corrected for *Lorentz* and polarization effects, and an absorption correction based on the multi-scan method [23] was applied in the cases of **16** and *trans*-**21**. Equivalent reflections were merged with the exception of the *Friedel* pairs of **18**. The structures were solved by direct methods using SHELXS97 [24] (for **16**) and SIR92 [25] (for **17**, **18** and *trans*-**21**), which revealed the positions of all non-H-atoms. In the case of **18**, there are two symmetry-independent molecules in the asymmetric unit. The atomic coordinates of the two molecules were tested carefully for a relationship from a higher symmetry space group using the program *PLATON* [26], but none could be found. In addition, both molecules are disordered by inversion of each entire molecule about its centre of gravity. Refinement of constrained site occupation factors for the two orientations of each molecule yielded values of 0.934(1) and 0.935(1) for the major conformation of molecules A and B, respectively. An extensive series of similarity restraints, was applied in order to keep the chemically equivalent bond lengths and angles about all atoms in the minor components similar to those of the major components. Furthermore, neighboring atoms within and between each disordered orientation were restrained to have similar atomic displacement parameters. The non-

[8]) CCDC-611000–611003 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the *Cambridge Crystallographic Data Center* via http://www.ccdc.cam.ac.uk/data_request/cif.

H-atoms of the major orientations were refined anisotropically, while those of the minor orientations were refined isotropically. The non-H-atoms of **16**, **17**, and *trans*-**21** were refined anisotropically. The amine H-atom of **16** was placed in the position indicated by a difference electron density map and its position was allowed to refine together with an isotropic displacement parameter. All remaining H-atoms of **16** and all of the H-atoms of **17**, **18**, and *trans*-**21** were placed in geometrically calculated positions and refined using a riding model where each H-atom was assigned a fixed isotropic displacement parameter with a value equal to 1.2 U_{eq} of its parent C-atom (1.5 U_{eq} for any Me group). The refinement of each structure was carried out on F^2 using full-matrix least-squares procedures, which minimized the function $\Sigma w(F_o^2 - F_c^2)^2$. Corrections for secondary absorption were applied, except in the case of **18**. In **16**, **17**, **18**, and *trans*-**21**, 1, 3, 8, and 2 reflections, respectively, whose intensities were considered as extreme outliers, were omitted from the final refinement. Refinement of the absolute structure parameter [27] for **18** yielded a value of 0.45(4), which indicates that the structure is an inversion twin. For **16**, the space group permits the compound to be enantiomerically pure, but the absolute configuration could not be determined. The enantiomer used in the refinement model was chosen arbitrarily. Neutral atom scattering factors for non-H-atoms were taken from [28a], and the scattering factors for H-atoms were taken from [29]. Anomalous dispersion effects were included in F_c [30]; the values for f' and f'' were those of [28b]. The values of the mass attenuation coefficients are those of [28c]. All calculations were performed using the SHELXL97 program [31].

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Legends

Fig. 1. *ORTEP Plot* [12] *of the molecular structure of* **16** (50% probability ellipsoids, arbitrary numbering of atoms)

Fig. 2. *ORTEP Plot* [12] *of the molecular structure of a)* **17** *and b) the major orientation of one of the symmetry-independent molecules of* **18** (50% probability ellipsoids, arbitrary numbering of atoms)

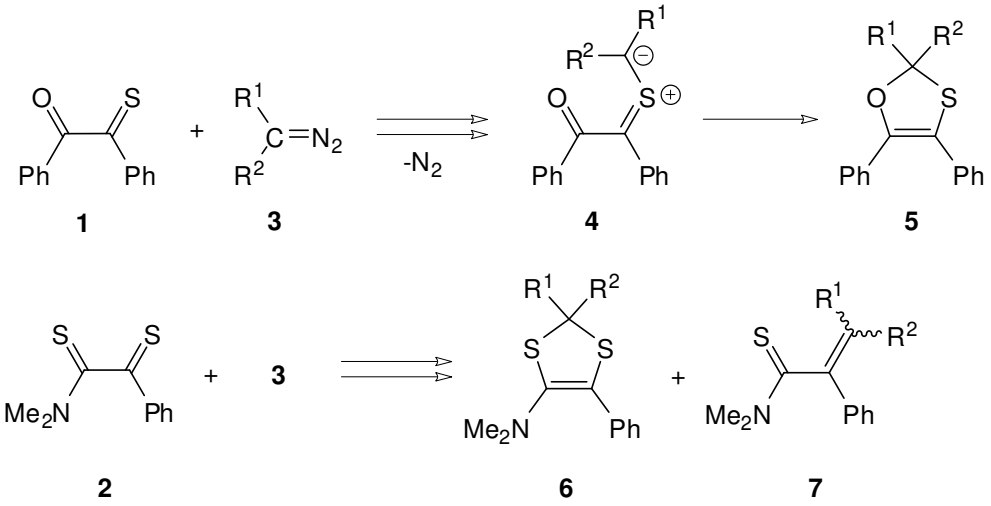
Fig. 3. *ORTEP Plot* [12] *of the molecular structure of trans*-**21** (50% probability ellipsoids, arbitrary numbering of atoms)

Table. *Crystallographic Data of Compounds* **16**, **17**, **18**, *and* trans-**21**.

	16	**17**	**18**	*trans*-**21**
Crystallized from	CH_2Cl_2/ Pentane	hexane/AcOEt /Et_2O	$CDCl_3$	CH_2Cl_2/hexane
Empirical formula	$C_{12}H_{18}N_2O_6$	$C_{23}H_{22}N_2$	$C_{23}H_{22}N_2S$	$C_{17}H_{18}N_2S$
Formula weight [g mol^{-1}]	286.28	326.44	358.50	282.40
Crystal color, habit	colorless, prism	colorless, prism	colorless, prism	colorless, prism
Crystal dimensions [mm]	0.22 × 0.25 × 0.32	0.10 × 0.15 × 0.22	0.10 × 0.15 × 0.25	0.20 × 0.22 × 0.30
Temperature [K]	160(1)	160(1)	160(1)	160(1)
Crystal system	orthorhombic	triclinic	monoclinic	monoclinic
Space group	$P2_12_12_1$	$P\bar{1}$,1	Cc	$P2_1/n$
Z	4	2	8	4
Reflections for cell determination	14502	4028	5653	34463
2θ range for cell determination [°]	4 – 55	4 – 55	4 – 60	4 – 60
Unit cell parameters a [Å]	7.8473(2)	9.9323(3)	12.9159 (1)	10.9672(2)
b [Å]	10.3424(2)	9.9977(3)	15.0573 (2)	6.0702(1)
c [Å]	17.3424(5)	10.4338(3)	20.1476 (2)	22.4345(4)
α [Å]	90	62.635(2)	90	90
β [°]	90	84.408(1)	106.6416(6)	91.248(1)
γ [Å]	90	78.997(1)	90	90
V [Å^3]	1407.51(6)	903.16(5)	3754.16(7)	1493.18(5)
D_x [g cm^{-3}]	1.351	1.200	1.268	1.256
μ(MoK_α) [mm^{-1}]	0.109	0.0703	0.181	0.208
Scan type	ϕ and ω	ϕ and ω	ω	ϕ and ω
$2\theta_{max}$ [°]	55	55	60	60
Transmission factors (min; max)	0.816; 0.925	–	–	0.870; 0.961
Total reflections measured	20739	21209	52142	38665
Symmetry-independent reflections	1867	4105	10265	4378
Reflections with $I > 2\sigma(I)$	1679	2953	8259	3218
Reflections used in refinement	1866	4102	10257	4376
Parameters refined; restraints	189; 0	229; 0	684; 1266	184; 0
R (on F; $I > 2\sigma(I)$ reflections)	0.0390	0.0483	0.0421	0.0449
wR (on F^2; all indept. reflections)	0.1050	0.1375	0.1000	0.1166
Weighting parameters [a, b][a]):	0.0578; 0.3696	0.0785; 0.0696	0.0506; 0.966	0.0533; 0.4053
Goodness of fit	1.066	1.045	1.024	1.062
Secondary extinction coefficient	0.032(6)	0.040(8)	-	0.069(4)
Final Δ_{max}/σ	0.001	0.001	0.001	0.001
$\Delta\rho$ (max; min) [e Å^{-3}]	0.28; -0.24	0.25; -0.22	0.24; -0.27	0.30; -0.27

[a]) $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = (F_o^2 + 2F_c^2)/3$.

Scheme 1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+
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R2
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S
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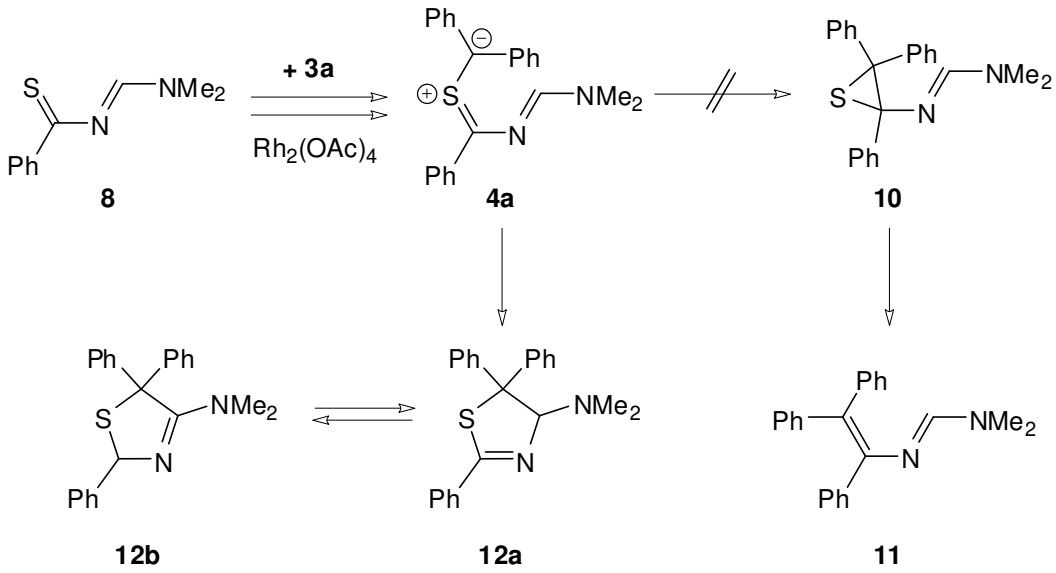
7

Scheme 2



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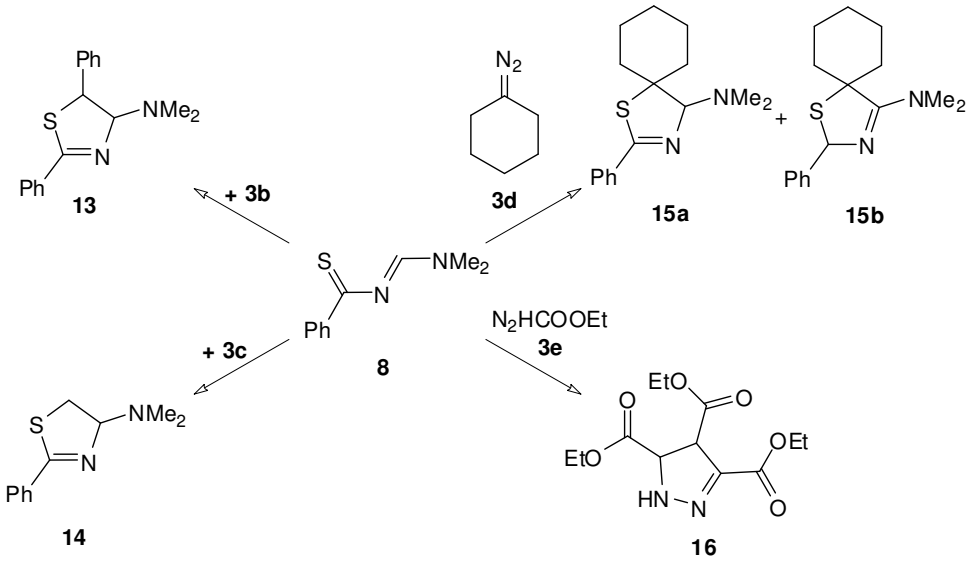
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N
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8
+ 3c
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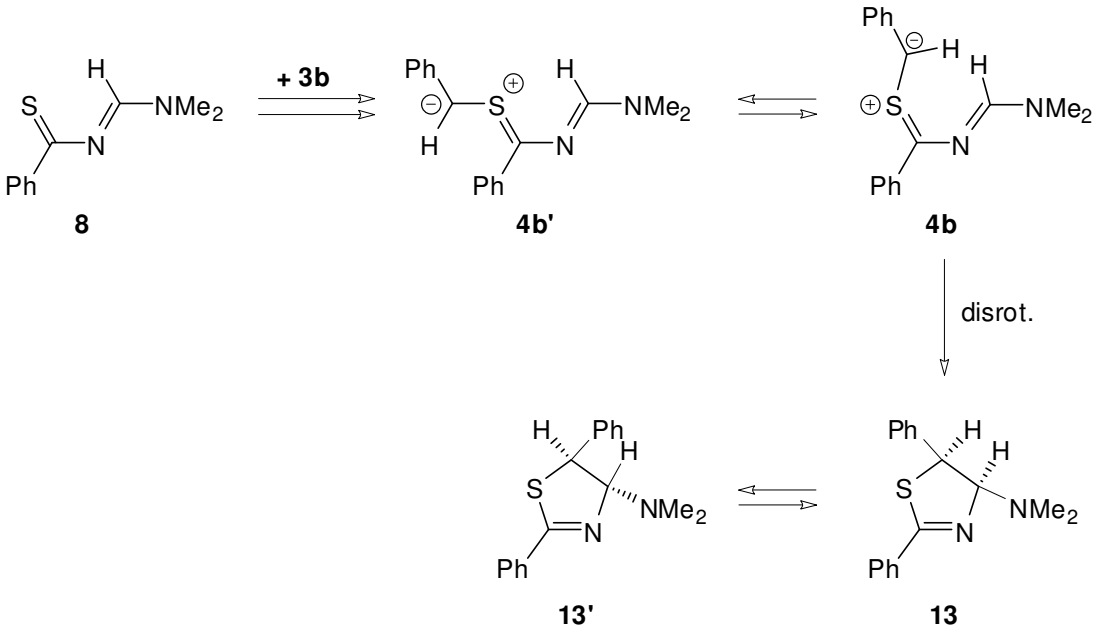
Scheme 4



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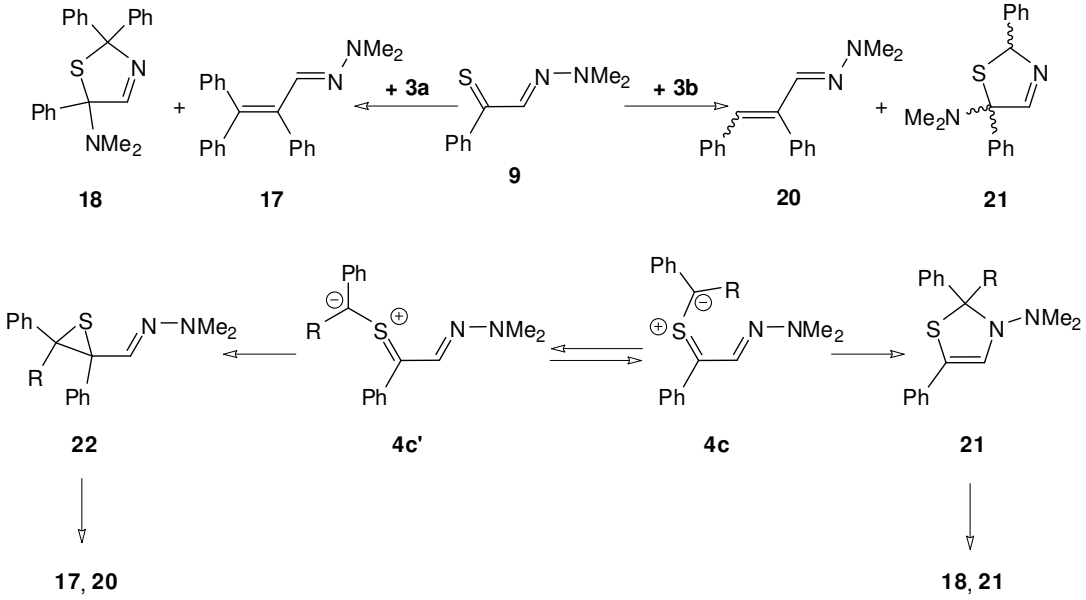
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17
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+ 3b
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N
Ph
Ph
20
+
Ph
S
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21
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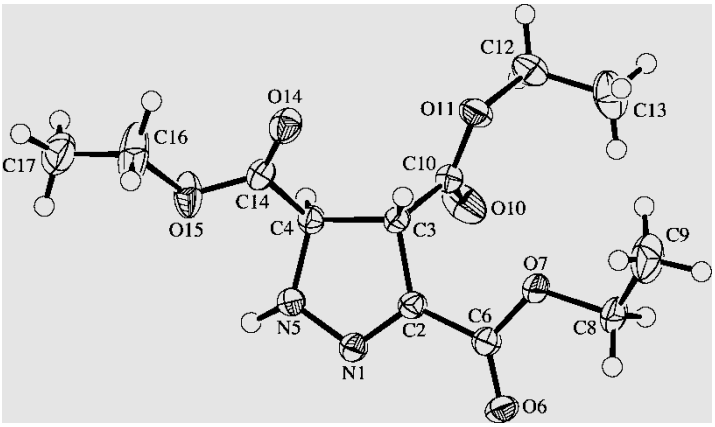
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C4
C3
C9
O15
O7
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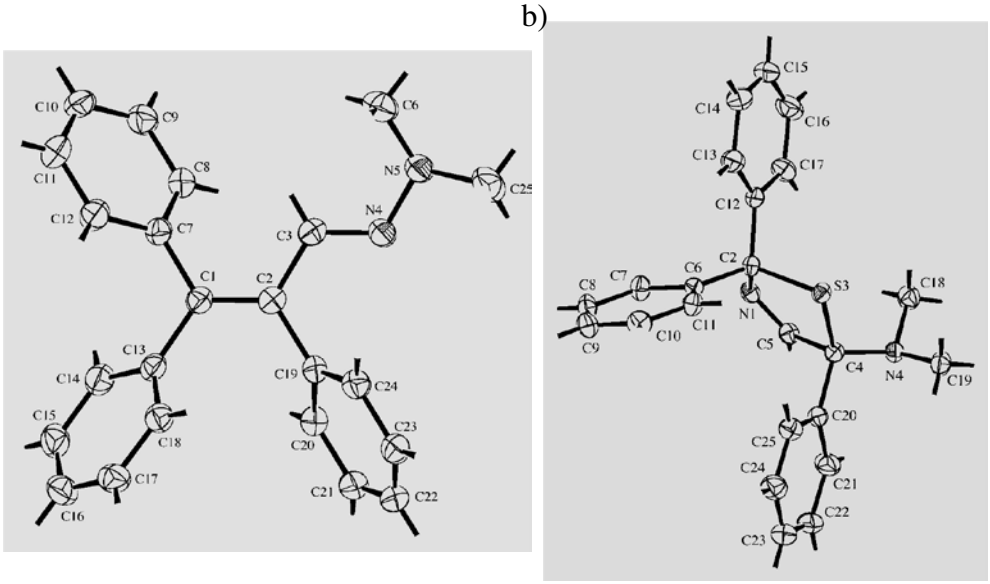
C2
C6
C8
N1
O6

Fig. 1

a) b)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C8
C12
C7
C1
C2
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N5
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C18
C16
C17
C19
C24
C20
C23
C21
C22
C15
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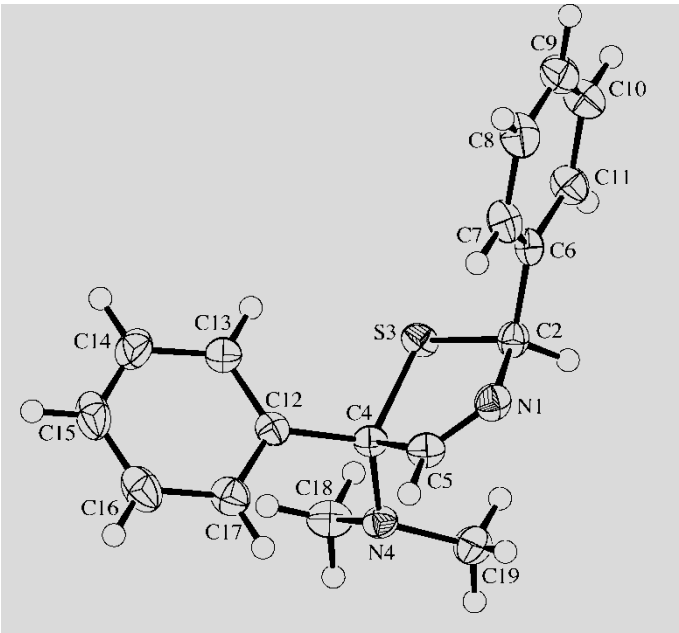
C16
C13
C17
C12
C2
C6
C7
C8
S3
C18
N1
C11
C9
C10
C5
C4
N4
C19
C20
C25
C24
C21
C22
C23

Fig. 2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C16
C17
N4
C19

Fig. 3

Chemical Abstract